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FOR MORE INFORMATION

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Influence of Aging and pH on Dissolution Kinetics and Stability of Pyromorphite

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Immobilization of metal contaminants in soil shows great potential as a cost-effective and environmentally friendly remediation technique. Lead-contaminated soils are typically removed from site and replaced with clean soil at great costs. Innovative technologies for sequestering lead in situ have been proposed and studied. One of these methods, called immobilization-remediation, seeks to both sequester most of the contaminant and retain the metal for the long-term. Scientists at the Environmental Protection Agency's Office of Research and Development in Cincinnati, Ohio, have examined how the most stable lead mineral, called chloropyromorphite, forms and dissolves over time, thus providing a better understanding of lead sequestration in soil.

Previous research has shown that adding phosphate materials to lead-contaminated soils leads to an environmentally stable and biologically inert lead mineral called chloropyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$). Because chloropyromorphite is the most stable lead mineral known, other solid-phase lead species should be transformed to chloropyromorphite by a dissolution-precipitation mechanism to immobilize soluble soil lead *in situ* by simply adding phosphate to the soil. But the long-term fate of immobilized lead as precipitated chloropyromorphite is not fully understood.

We investigated the kinetics of dissolution and crystallization dynamics of synthetic chloropyromorphites with increasing aging times ranging from one hour to one year, to understand better what may be happening in the field setting. The chloropyromorphites were dissolved in a solution containing not only phosphoric acid, but also nitric acid, thus simulating environmental conditions one may find in areas ranging from acid mine drainage to agricultural soil settings.

The objectives of this research were to understand the effect of aging time on the stability of chloropyromorphite dissolved in phosphoric and nitric acid, to examine physical and chemical alterations of the chloropyromorphite samples, and to model the kinetic data collected from the dissolution experiments. Aging of the samples prior to dissolution was investigated by using x-ray absorption fine structure (XAFS) and x-ray diffraction (XRD) spectroscopies, and the stability of the chloropyromorphite material with temperature was studied with high-resolution thermogravimetric analysis (HRTGA).



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Figure 1 shows data for XAFS, XRD, and HRTGA analyses of aged chloropyromorphite prior to dissolution. The XAFS data (**Figure 1a**, solid line), collected at beamline X11A of the National Synchrotron Light Source (NSLS), show relatively little difference between the one-hour and one-year samples.

These same chloropyromorphite samples were also examined by XRD (**Figure 1b**) and, again, do not suggest any alteration in the chemistry or crystallinity of the chloropyromorphite phases as aging time increases. But HRTGA showed that aging of the chloropyromorphite crystals did change with increasing residence time (**Figure 1c**), suggesting, perhaps, an increase in the crystals' Ostwald ripening, in which small crystals, more soluble than large ones, dissolve and re-precipitate onto larger particles.

The dissolution experiments conducted for this research were designed to observe and compare data as influenced by aging time, pH (potential Hydrogen) of the dissolution agent (the pH describes the hydrogen-ion activity of the solution, and determines if the so-

lution is acid, basic or neutral), and dissolution method (stirred flow or mixing in batches, instead of continuously, also called batch method).

Regardless of pH or dissolution method, it appeared that the one-hour-aged chloropyromorphite was the most soluble. Aging of chloropyromorphite from one day to one year did not lead to a significant increase in stability, suggesting that crystal aging was accomplished within 24 hours.

We also observed that, as the pH of the nitric acid decreased, the

amount of released lead increased. By removing the dissolution reaction products in the stirred-flow experiments, more chloropyromorphite was dissolved in the stirred-flow than in the batch studies, the difference in released lead between these two methods becoming more pronounced as pH increased. So, once chloropyromorphite forms in contaminated soils and sediments, it should remain immobilized and stable in these environments under near-neutral pH.

The potential impact of stabilization remediation methods to safely

sequester metal contaminants in the natural environment holds great promise but must be managed carefully and intelligently. The results of this work and of others demonstrate that chloropyromorphite formation can be easily accomplished by the reaction of available lead and phosphorus. Our study suggests that chloropyromorphite's persistence would endure most environmental conditions, thus making lead-immobilization via phosphorus an ideal remediation mechanism.

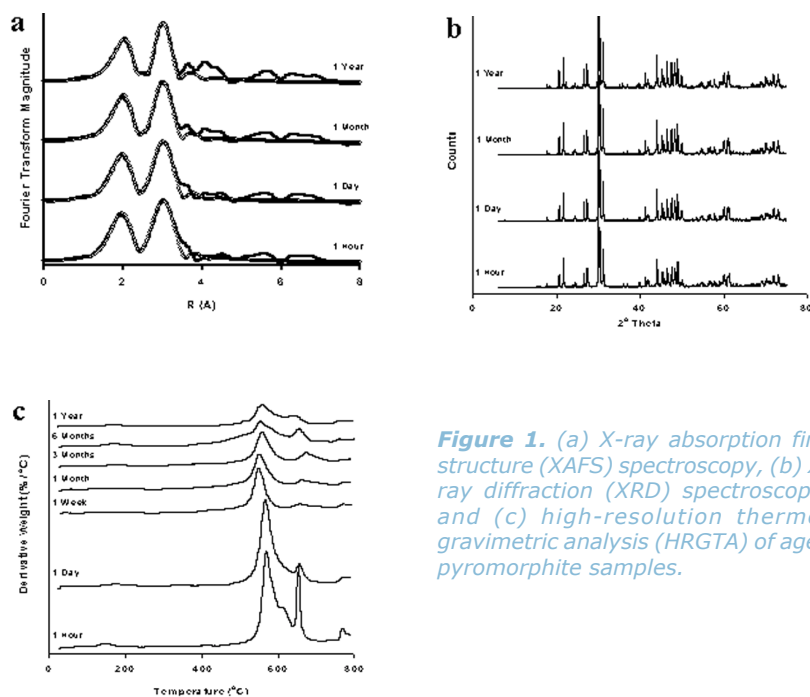


Figure 1. (a) X-ray absorption fine structure (XAFS) spectroscopy, (b) X-ray diffraction (XRD) spectroscopy, and (c) high-resolution thermogravimetric analysis (HRGTA) of aged pyromorphite samples.

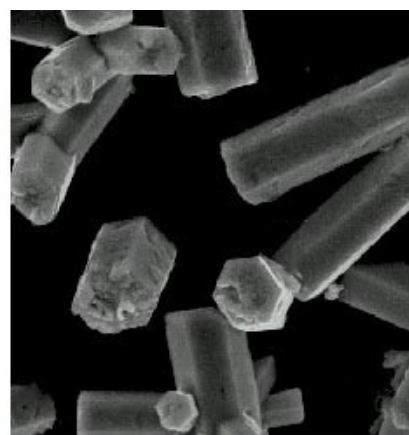


Figure 2. Crystals of chloropyromorphite.